# Analysis of quasi-reversible CVs and dEIS data:
Transformation to potential-program independent forms

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Dynamic electrochemical impedance spectroscopy, dEIS, comprises repetitive impedance spectrum measurements while slow scan-rate voltammetry is running. Its main virtue is the short measurement time, reducing the danger of contamination of the electrode surface. To further the use of dEIS, we have recently elaborated a set of theories aimed at the related data processing for three groups of fundamental electrode reactions: diffusion-affected charge transfer, charge transfer of surface-bound species, and adsorption–desorption. These theories yielded equations by which the voltammograms can be transformed to potential program invariant forms, allowing an easy calculation of the system parameters like rate coefficients; similar equations have been derived for the potential dependence of equivalent circuit parameters obtained from the impedance spectra. These derivations have also been presented in a single, unified one [1]. An example is shown in the figure: From a set of "quasi-reversible" CVs taken at varied scan-rates v, two scan-rate independent, hysteresis-free functions can be calculated. One of them is the diffusion-free polarization curve, $j_{inf}(E)$, the other is the semi-integrated form of the reversible CV, $M_{rev}(E)$.
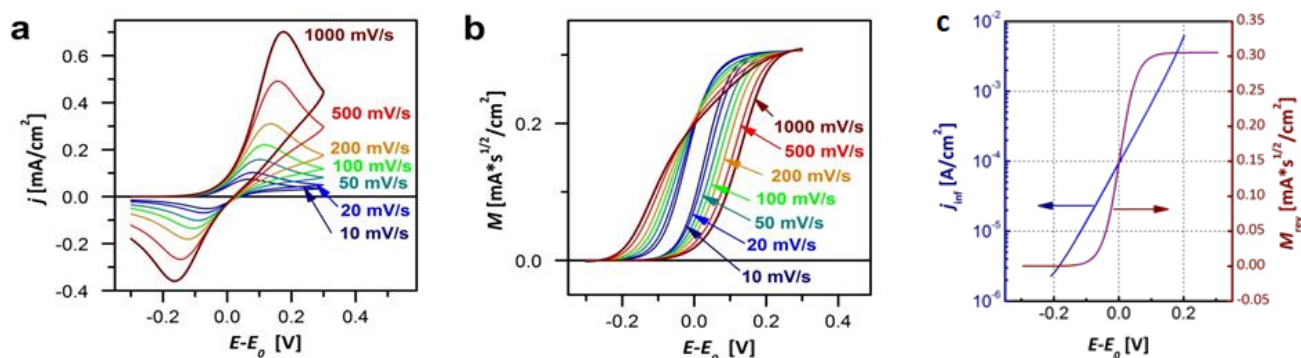
Simulated CVs of a diffusion affected charge transfer reaction with varied scan rates (a), their semiintegrals (b), and the calculated j_{inf} and M_{rev} functions (c). Simulation parameters: $D_{red} = D_{ox} = 10^{-5}$ cm^2/s, $c_{red} = 10^{-6}$ mol/cm^3, $c_{ox} = 0$ mol/cm^3, $E_0 = 0$, $k_0 = 0.001$ cm/s, $\alpha = 0.5$.

The theory is recommended to evaluate electrode kinetic measurements, particularly when the potential dependence of rate coefficients is under study. Implications to electroanalytical chemistry are also involved.

References

1. T. Pajkossy, Determination of Electrode Kinetics Parameters from Dynamic Electrochemical Impedance, Spectroscopy Measurements via Potential-Program Invariant Function, *J. Phys. Chem. Lett.* **14(47)** 2023 10599–10608 https://doi.org/10.1021/acs.jpclett.3c02810